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## EUROPEAN PATENT APPLICATION

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*FLEXIBLE COMPOSITE PIPE FOR HIGH TEMPERATURE FLUIDS + 1985  
VINYLIDENE FLUORIDE WITH ~~CHLORINE~~ REINFORCING HEXAFLUORO PROPYLENE COPOLYMER  
AND WHICH IS largely free of cracking at low temperatures or frequent bending.*

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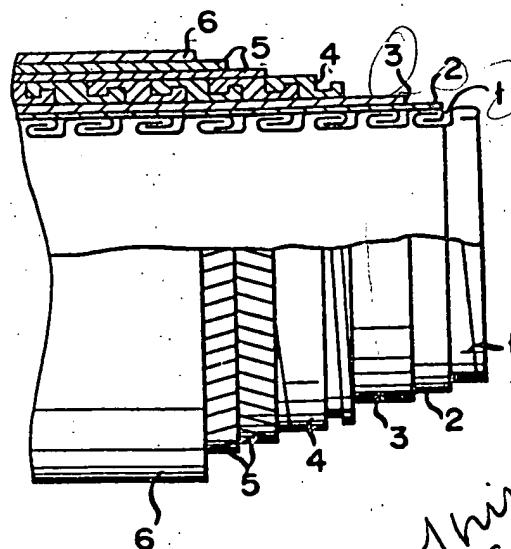
㉑ Flexible composite pipe for high-temperature fluids.

㉒ A flexible composite pipe for transporting a high-temperature fluid of the invention has an inner pipe (3) for passing a high-temperature, high-pressure fluid therethrough, a reinforcing layer (4, 5) formed around the inner pipe (3), and a protective sheath layer (6) formed around the reinforcing layer (4, 5). The inner pipe consists of a material which is selected from a polyvinylidene fluoride copolymer resin, a blend thereof with a polyvinylidene fluoride resin, or a composition based on the polyvinylidene fluoride copolymer resin and which has, when hot pressed into a sheet, an Izod impact strength of 10 kg-cm/cm or more and an apparent Young's modulus in tension of 90 kg/mm<sup>2</sup> or less.

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period of time.

Heat-resistant resins to replace nylon resins generally include fluorine containing plastics and various engineering plastics. However, none of such 5 resins satisfies all the requirements as to elongation, stress cracking and the like in order to manufacture high-temperature, high-pressure flexible transport pipes.

More specifically, polyvinylidene fluoride 10 resins are known to have excellent extrudability, heat-resistance and chemical resistance and are used for pipe lining and for solid pipes. However, such resins have not been applied in the manufacture of 15 flexible pipes, excluding extremely small diameter pipes.

The reason can be attributed to the high rigidity 20 of polyvinylidene fluoride resins. When such a resin is used for purposes of the present invention, as the pipe is cut with a saw or the like in a bent state or in a straightened state after having been bent, cracks run for several tens of meters, particularly in wintertime, due to low temperatures. For this reason, 25 polyvinylidene fluoride resins cannot be used in practice.

Cracking of polyvinylidene fluoride resins is 30 also considered to be attributable to a high molding shrinkage of the resins and resultant large residual strain of a formed body, in addition to inherent high rigidity. In order to confirm this consideration, a pipe was manufactured by extrusion coating a polyvinylidene fluoride resin directly on a flexible 35 interlocked metal pipe obtained by interlocking metal strips. When a notch was formed in the pipe, crack propagation from the notch was observed. It was demonstrated as a result of this test that cracks were formed from the recessed portions (projections in the resin formed body) at the engaging portions of the metal

strips of the interlocked pipe.

It is a main object of the present invention to provide a flexible composite pipe for use at high temperatures and high pressures.

5 It is another object of the present invention to provide a flexible composite pipe which can be used at high temperatures and which does not allow propagation of cracks upon being bent or upon formation of notches.

10 It is still another object of the present invention to provide a high-temperature, high-pressure flexible composite pipe which does not cause extension of an inner pipe into surrounding reinforcing strips at high temperatures, so that the pipe can be used over a long period of time.

15 It is still another object of the present invention to provide a high-temperature, high-pressure flexible composite pipe which is not influenced by being bent repeatedly.

The present invention has been established based on 20 various studies and tests including the one described above by the present inventors and provides a fluid transport pipe consisting of an inner pipe for allowing passage therein of a desired fluid at a high temperature and at a high pressure, a reinforcing layer formed around the inner pipe, and a protective sheath layer 25 coated around the reinforcing layer, the inner pipe being obtained by extruding a polyvinylidene fluoride copolymer resin, a blend thereof with a polyvinylidene fluoride resin or a composition based on the polyvinylidene fluoride copolymer resin which has, when 30 hot-pressed into a sheet, an Izod impact strength of 10 kg-cm/cm or more and an apparent Young's modulus in tension of 90 kg/mm<sup>2</sup> or less.

This invention can be more fully understood from 35 the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a side view of a flexible composite pipe.

according to an embodiment of the present invention, wherein the upper half is shown in section and the lower half is shown to expose each different layer of the pipe;

5 Fig. 2 is a side view of a flexible composite pipe according to another embodiment of the present invention, wherein the upper half is shown in section and the lower half is shown to expose each different layer of the pipe; and

10 Fig. 3 is a cross-sectional view of the composite pipe shown in Fig. 2.

In the first embodiment shown in Fig. 1, an inner pipe 3 is arranged around a resin tape layer 2 formed by winding a resin tape around an interlocked pipe 1 of steel or stainless steel. Reinforcing layers 4 and 5 and a protective sheath layer 6 are formed around the inner pipe 3. The inner reinforcing layer 4 is formed by winding Z-shaped metal strips at a short pitch such that they are interlocked with each other. The outer reinforcing layer 5 consists of two layers of flat metal strips which are wound at a long pitch and in opposite directions.

25 In another embodiment of the present invention shown in Fig. 2, an inner pipe 3 is directly coated on a steel or stainless steel interlocked pipe 1. An outer layer 7 of a resin having a rigidity at high temperatures which is higher than that of a resin of the inner pipe 3 is formed therearound. Inner and outer reinforcing layers 4 and 5 are formed around the outer layer 7. The inner reinforcing layer 4 comprises two interlocked layers of U-shaped steel strips. The outer reinforcing layer 5 comprises two layers of flat steel strips. A plastic protective sheath layer 6 is formed as an outermost layer.

30 35 The inner pipe 3 comprises an extruded pipe of a resinous material which has, when hot pressed into a sheet, an Izod impact strength of 10 kg-cm/cm or more

and an apparent Young's modulus in tension of 90 kg/mm<sup>2</sup> or less. The resinous material is a polyvinylidene fluoride copolymer resin, a blend thereof with a polyvinylidene fluoride resin, or a composition based 5 on the polyvinylidene fluoride copolymer resin.

According to the present invention, the inner pipe consists of one of the above-mentioned resinous materials for the following reasons. When a resinous material has an Izod impact strength lower than 10 kg-cm/cm, the 10 pipe has too low an impact strength. When the apparent Young's modulus in tension exceeds 90 kg/mm<sup>2</sup>, cracking or tearing occurs.

The "polyvinylidene fluoride copolymer resin" used herein is a resin mainly consisting of a vinylidene fluoride monomer and obtained by copolymerizing one 15 or more of comonomers such as tetrafluoro ethylene monomer, 3-fluoro-1-chloro ethylene monomer, or hexafluoro propylene monomer. A copolymer consisting of 5 to 10% mole of hexafluoro propylene monomer and 20 the balance of vinylidene fluoride is particularly preferable due to its good physical properties.

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When the material to be used for the inner pipe is defined above, the Izod impact strength of the material is defined as that of a sample piece of a sheet obtained by hot pressing the material. This is because 25 preparation of this sample piece by hot pressing is easy and relatively small measurements are obtained when the hot pressed sheet is subjected to measurement.

In a fluid transport composite pipe according to 30 the present invention, a flexible interlocked metal pipe 1 obtained by interlocking metal tapes is inserted within the inner pipe 3. When the composite pipe is intended for use at a location where high pressure resistance is required, e.g., deep sea, the interlocked 35 metal pipe preferably has a plastic tape layer 2 wound therearound.

The reason for this is as follows. The interlocked

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portions of the metal tapes are in recessed form. When an inner pipe is directly extruded around the metal pipe having such recessed interlocked portions, the inner pipe material extends into the recessed portions. Then, depending upon the type of the inner pipe material, the thickness of the inner pipe and the like, the extended parts of the inner pipe at the recessed interlocked portions may be sources of cracking or the like in the inner pipe.

10 The reinforcing layers 4 and 5 formed around the inner pipe 3 according to the present invention impart a resistance to internal pressure of the composite pipe. The layers 4 and 5 normally comprise tapes, bands, strips or wires of metal or reinforced plastics.

15 When the reinforcing layers comprise at least one reinforcing layer obtained by winding a profile strip at a short pitch and at least two reinforcing layers wound at a long pitch in opposite directions, the former reinforcing layer imparts a resistance to internal pressure mainly along the circumferential direction of the composite pipe, while the latter two reinforcing layers impart a resistance to internal pressure along the axial direction of the composite pipe.

20 When the material for reinforcing layers is FRP strips with many ribs, proper spaces can be formed between the reinforcing layers. When such spaces are formed in the pipe, undesirable cooling from the external environment can be prevented.

25 As described above, an inner pipe is obtained from a resinous material having, when hot pressed into a sheet, an Izod impact strength of 10 kg-cm/cm or more and an apparent Young's modulus in tension of 90 kg/mm<sup>2</sup> or less. The resinous material is a polyvinylidene fluoride copolymer resin, a blend thereof with a polyvinylidene fluoride resin, or a composition based on the polyvinylidene fluoride copolymer resin. Reinforcing layers and an outer protective sheath layer are formed

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around the inner pipe to provide a flexible composite pipe resistant to high temperatures and high pressures. When the thickness of strips used for the reinforcing layer is large or when the composite pipe is expected to 5 be exposed to repeated bending stress, an outer layer 7 consisting of a resin having a rigidity at high temperatures which is higher than that of the resin of the inner pipe 3 at the same temperature is preferably formed therearound.

10 The reason for this is as follows. Although a polyvinylidene fluoride resin has an excellent thermal stability, it has a considerably small strength at high temperatures. When a high internal pressure acts on the composite pipe, the inner pipe material extends 15 into gaps between the surrounding reinforcing layers consisting of wires, thereby forming ribs. When the composite pipe is subjected to bending stress in this state, stress concentration occurs at the proximal portions of the ribs, causing cracking of the inner 20 pipe or separation of the ribs.

In view of this problem, the outer layer serves to prevent the polyvinylidene fluoride resin from extending 25 into the gaps between the reinforcing layers. The outer layer according to the present invention can be formed by directly extruding a polyamide resin such as nylon 6, nylon 6-6, nylon 11, nylon 12 or nylon copolymer; or a resin such as polyamide elastomer or thermoplastic polyester elastomer. The outer layer can alternatively 30 be obtained by gap winding (edges are separated to form gaps) or lap winding (edges overlap each other) a thin metal tape or a film of polyester or nylon or a cloth material such as canvas cloth or glass tape. Preferably at least two layers of a metal such as steel, stainless steel, copper or nickel can be used as the outer layer 35 by gap-wounding so that gaps of each layer are covered by each overlying layer.

When the high-temperature, high-pressure flexible

composite pipe according to the present invention is intended for use where it is subject to repeated bending stress, it is preferable that a grease be injected in the inner and outer reinforcing layers and a plastic film be inserted therebetween.

When the composite pipe not treated as mentioned above is subject to repeated bending stress, the two reinforcing layers shift relative to each other and wear due to high internal pressure. The reinforcing layers thus undergo wear and fatigue and may be damaged.

The present invention will now be described by way of its Examples and Comparative Examples.

Example 1

A vinylidene fluoride monomer and 3-fluoro-1-chloro ethylene monomer were reacted in a ratio of 9 : 1 to obtain a polyvinylidene fluoride copolymer resin (when hot pressed into a sheet it had an Izod impact strength of 11.6 kg-cm/cm and an apparent Young's modulus in tension of 56.8 kg/mm<sup>2</sup>). The copolymer resin was extruded to form an inner pipe having an inner diameter of 2 inches and a thickness of 4 m/m. Iron strips having a width of 50 mm were wound around the inner pipe to form two reinforcing layers respectively having thicknesses of 0.6 m/m and 1 m/m such that each layer had a gap distance of 5 m/m. Iron wires having a diameter of 6 m/m were wound therearound in two layers in different directions at angles of 15 degrees. A low density polyethylene was extruded therearound to a thickness of 4 m/m as a protective sheath layer to complete a composite pipe.

In the above manufacturing process, the inner pipe of the polyvinylidene fluoride copolymer resin was wound around a drum having a diameter of 1 m a total of 6 times. However, the inner pipe suffered no abnormality.

The composite pipe obtained had an internal breakdown pressure of 500 kg/cm<sup>2</sup>.

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Comparative Example 1

Polyvinylidene fluoride (when hot pressed into a sheet it had an Izod impact strength of 7.2 kg-cm/cm and an apparent Young's modulus in tension of 88.2 kg/mm<sup>2</sup>) was extruded into a pipe having the same size as that in Example 1 so as to manufacture a composite pipe as in Example 1. However, when the pipe was wound around the drum for the first time before winding iron strips, the pipe cracked.

Examples 2 - 4 & Comparative Example 2

Resins and resin compositions of Examples 2 to 4 and Comparative Example 2 in the Table below were extrusion coated to a thickness of 3 m/m on interlocked pipes made from SUS 304 having a diameter of 1 inch. The inner pipe was bent at a radius of curvature of 22 cm to form a notch having a length of about 2 cm and propagation of cracks was checked. The obtained results are also shown in the Table below. When the pipe did not crack, the pipe was straightened and bent at a radius of curvature R of 22 cm. The bending/straightening cycle was repeated to a maximum of 20 times. The obtained results are shown together with the results of the Izod impact strength test of a separately prepared hot pressed sheet and the results of the Young's modulus in tensile test of a 1 mm thick sheet. Data on repeating time is the minimum value before crack propagation when five samples were tested.

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Table

	Resin (trade name)	Crack	Repeat- ing time	Izod impact strength (kg-cm /cm)	Young's modulus in ten- sion (kg/mm <sup>2</sup> )
5	Example 2  Polyvinylidene fluoride co-polymer resin ("Kynar-2800" available from Pennwalt Corp., U.S.A.)	None	20 times	39	54
10	Example 3  Polyvinylidene fluoride co-polymer ("Solef-11010" available from Solvay Co., Belgium)	None	20 times	16	60
15	Example 4  1 : 1 blend of "Kynar-2800" with "Kynar-460"	None	20 times	16	57
20	Comparative Example 2  Polyvinylidene fluoride resin ("Kainer-460" available from Pennwalt Corp., U.S.A.)	Cracks formed	0	5.1	77
25					

In the Izod impact strength test, samples each had a thickness of 6 mm.

The Young's modulus in tension was determined by referring to an initial slope of a stress-strain characteristic curve (23°C) which was obtained by punching a No. 2 dumbbell from a 1 mm thick sheet, and pulling it at a rate of 50 mm/min.

#### Example 5

A polyester tape was wound in a plurality of layers to a total thickness of 0.5 m/m around the interlocked pipe having a diameter of 1 inch as in Example 2,

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thereby forming a plastic tape layer surrounding the recessed interlocked portions of the interlocked pipe. A polyvinylidene fluoride copolymer resin ("Foraflon 650HD" (trade name); having an Izod impact strength of 11 kg-cm/cm and an apparent Young's modulus in tension of 88 kg/mm<sup>2</sup>) was extruded around the plastic tape layer to a thickness of 3 m/m to form a pipe, i.e., an inner pipe. The inner pipe was subjected to the same tests as in Examples 2 to 4 and was found to form no cracks after 10 bending cycles.

When the resin as in Comparative Example 2 was formed in a similar manner, cracks formed after 6 bending cycles.

When the polyester film or the like is wound around a flexible metal pipe, i.e., an interlocked pipe, it prevents the surrounding polyvinylidene fluoride copolymer from extending into the recessed interlocked portions of the interlocked pipe. When the polyester film or the like is wound in a plurality of layers, it provides a cushion effect. Therefore, when the pipe is bent, local strain of the resin is not caused, and residual strain is cancelled.

Example 6

A polyester tape was wound in a plurality of layers to a total thickness of 0.5 mm around an interlocked pipe the same as that used in Example 2 except that it had a diameter of 3 inches. The same inner pipe as that used in Example 2 having a thickness of 6 m/m was arranged therearound. Steel strips having U-shaped sections (U strips) were wound in two layers such that recesses and ribs of the respective layers engaged with each other. The two layers had a total thickness of 6 m/m. Two layers of flat steel strips having a thickness of 3 mm were wound therearound at an angle of 40 degrees at opposite direction. A resin protective sheath layer consisting of a low-density polyethylene was coated.

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Oil heated to a temperature of 120°C was circulated in the composite pipe prepared in this manner. After the pipe reached equilibrium, internal pressure breakdown test was performed. The pipe broke at an 5 internal breakdown pressure of 950 kg/cm<sup>2</sup>. The pipe had a surface temperature of 50°C when this measurement was obtained.

When an attempt was made to prepare a composite pipe as in this Example using the resin of Comparative 10 Example 2, cracks were formed along the longitudinal direction of the pipe when the pipe was cut before the U-shaped strips 4 were wound.

Example 7

A composite pipe was prepared. The pipe had a 15 similar structure to that in Example 6 except that the resin of an inner pipe 3 was the same as that used in Example 3 and cross-shaped FRP strips having the same cross-sectional area were used in place of the flat steel strips 4 having a thickness of 3 mm. When the 20 pipe was subjected to the same tests as in Example 6, the pipe had an internal breakdown pressure of 850 kg/mm<sup>2</sup>. When the pipe broke, it had a surface 25 temperature of 38°C and had a better temperature retention property than that of the pipe in Example 6.

Example 8

A polyvinylidene fluoride copolymer resin ("Kynar 2800" (trade name)) was coated around an interlocked pipe made from SUS 304 having an inner diameter of 76 mm and an outer diameter of 83.5 mm to form an inner pipe 30 having an inner diameter of 83.5 mm and an outer diameter of 89.5 mm. A thermoplastic polyester elastomer ("Hytrel 7246" (trade name)) was extrusion coated therearound to form an outer layer having an inner diameter of 89.5 mm and an outer diameter of 95.5 mm. 35 U-shaped steel strips (10 mm wide, 4 mm thick) were wound in two layers at a pitch of 10.5 mm so that the respective layers engaged with each other. Shell Darina

2 grease is injected in the two layers. The first retinforcing layer thus formed had an inner diameter of 95.5 mm and an outer diameter of 111.5 mm. High density polyethylene film which is 60 µm thick and 50 mm wide is wound in half lap in two layers so that the total outer diameter becomes 112.0 mm. Flat steel strips (8 mm wide, 3 mm thick) were wound therearound in two layers and the same manner mentioned above between two layers and the same grease injected in the layers. The second retinforcing layer thus obtained had an inner diameter of 120.0 mm and an outer diameter of 124.5 mm. A resin 120° C was injected in the gap between the two layers and the same grease injected in the layers. The second protective sheath layer was finally formed to complete a composite pipe.

The composite pipe was cut into a length of 3 m and the repeatable bending test of the pipe was performed by circulating oil at a temperature of 120°C inside the pipe, applying a pressure of 210 kg/cm<sup>2</sup>, and repeating bending the pipe at a radius of curvature of 2 m at 25 rpm. No abnormality was observed up to 1 x 10<sup>4</sup> cycles.

When oil at a temperature of 120°C was circulated in the composite pipe of this example and an internal pressure was applied after the sample surface temperature saturated, oil leakage occurred at an internal pressure of 1,900 kg/mm<sup>2</sup>. When the composite pipe was disassembled, the thermoplastic polyester was extended into the outer layer was observed to have elastomer of the outer layer was noted.

**Claims**

1. A flexible composite pipe for transporting a high-temperature fluid, comprising:
  - an inner pipe (3) consisting of a pipe obtained by extruding one member selected from the group consisting of polyvinylidene fluoride copolymer resins, blends thereof with polyvinylidene fluoride resins, and compositions based on the polyvinylidene fluoride copolymer resins, which have, when hot pressed into a sheet, an Izod impact strength of not less than 10 kg-cm/cm and an apparent Young's modulus in tension of not more than 90 kg/mm<sup>2</sup>;
  - a reinforcing layer (4, 5) formed around said inner pipe; and
  - a protective sheath layer (6) coated around said reinforcing layer.
2. A flexible composite pipe according to claim 1, further comprising an outer layer (7) which is formed around said inner pipe (3) and which consists of a resin having a rigidity at high temperatures which is higher than that of the material of said inner pipe.
3. A flexible composite pipe according to claim 2, characterized in that the resin of said outer layer having a rigidity at high temperatures which is higher than that of the material of said inner pipe is one member selected from the group consisting of a polyester elastomer and a polyamide resin.
4. A flexible composite pipe according to claim 1, further comprising an outer layer (7) which is formed around said inner pipe and which consists of gap-wound thin metal tape in at least two layers such that gaps of each layer of said thin metal tape are covered by each overlying layer.
5. A flexible composite pipe according to claim 1, 2 or 4, further comprising a plastic tape layer (2) wound around a flexible interlocked pipe (1) obtained by

interlocking metal strips; and wherein said reinforcing layer (4, 5) formed around said inner pipe (3) is obtained by winding a wire, a strip or a band of a metal or a fiber reinforced plastic.

5. A flexible composite pipe according to claim 5, characterized in that said reinforcing layer (4, 5) consists of a profile reinforcing strip wound at a short pitch, and flat reinforcing strips wound in different directions in at least two layers at a long pitch.

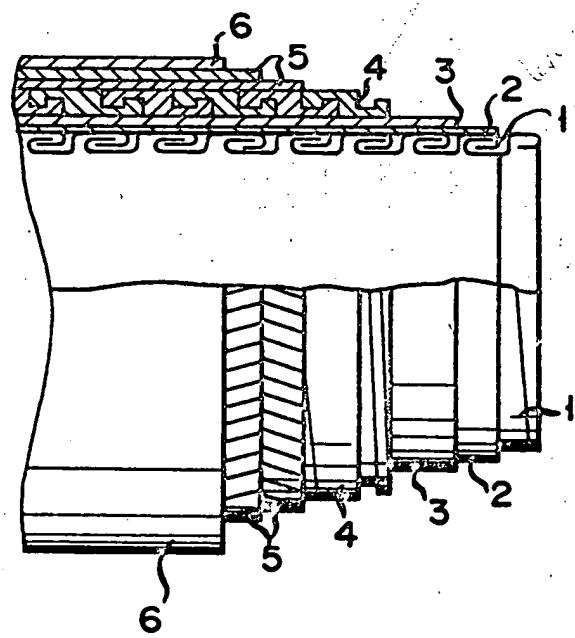
10. A flexible composite pipe according to claim 6, characterized in that said reinforcing layer (4, 5) consists of fiber reinforced plastic reinforcing layers, and said reinforcing strips wound at the long pitch have a section with a number of ribs.

15. A flexible composite pipe according to claim 5 or 6, characterized in that said reinforcing layer (4, 5) comprises two, inner and outer reinforcing layers, and a grease is injected in said inner and outer reinforcing layers (4, 5) and a plastic film is inserted  
20 therebetween.

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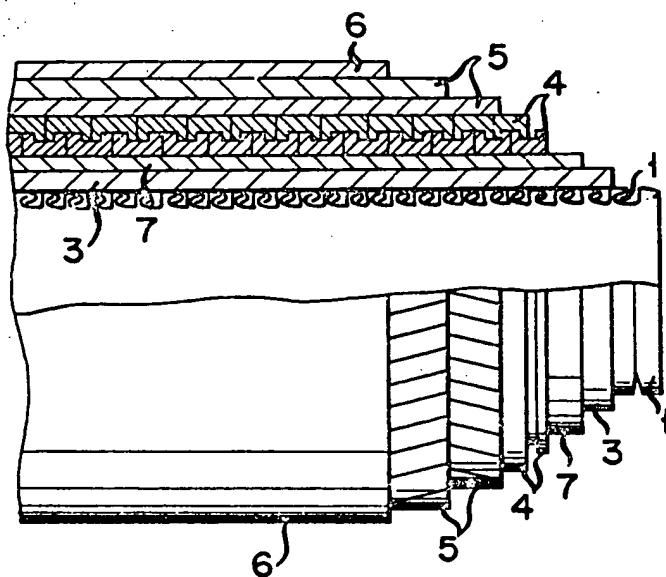
FIG. 1



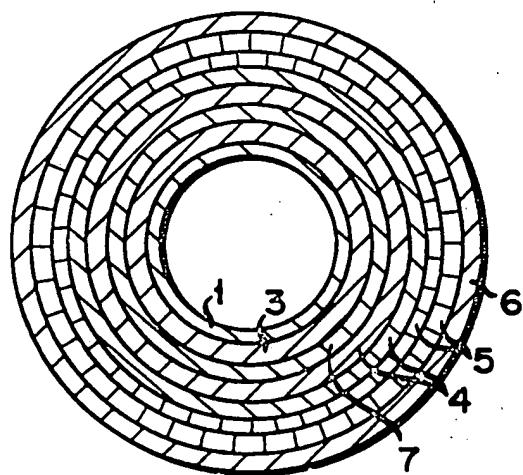
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F I G. 3



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